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DIASTEREOSELECTION AND THE INFLUENCE OF CHIRAPHOS ON  
METAL-CENTERED CHIRAL. (U) ROCHESTER UNIV NY DEPT OF  
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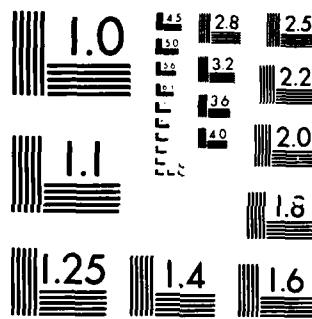
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Contract N00014-83-K-0154

Task No. NR 634-742

TECHNICAL REPORT NO. 9

Diastereoselection and the Influence of Chiraphos on Metal-Centered Chirality  
in Cis Oxidative Addition of Hydrogen and Triphenylsilane

by

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Prepared for Publication

in the

Journal of the American Chemical Society

University of Rochester

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January 20, 1986

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REPORT DOCUMENTATION PAGE		READING INSTRUCTIONS BEFORE COMPLETING FORM	
1. REPORT NUMBER	2. GOVT ACCESSION NO	3. RECIPIENT'S CATALOG NUMBER	4. TYPE OF REPORT & PERIOD COVERED Interim Technical Report
4. TITLE (and Subtitle) Diastereoselection and the Influence of Chiraphos on Metal-Centered Chirality in the Oxidative Addition of Hydrogen and Triphenylsilane	5. NAME OF CONTRACTING ORGANIZATION University of Rochester		
7. AUTHOR(S) Anatoli J. Kuntin, Kamy Farid, Curtis E. Johnson and Richard E. Eisenberg	8. CONTRACT OR GRANT NUMBER(S) N00014-83-K-0154		
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry University of Rochester Rochester, New York 14627		10. PROGRAM ELEMENT, PROJECT, TASK AND WORK UNIT NUMBERS NR 034-742	
11. CONTRACTING ORGANIZATION NAME AND ADDRESS Office of Naval Research Department of the Navy Arlington, Virginia 22217		12. REPORT DATE January 20, 1986	
13. NUMBER OF PAGES 8		14. SECURITY CLASS. (or this report) Unclassified	
15. SECURITY CLASSIFICATION SOURCE (Contracting Office)		16. SECURITY CLASSIFICATION SOURCE (Sponsoring Organization)	
17. DISTRIBUTION STATEMENT (or this Report) This document has been approved for public release and sale; its distribution is unlimited.			
18. PREPARED FOR PUBLICATION IN JOURNAL OF THE AMERICAN CHEMICAL SOCIETY			
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Oxidative addition; Stereoselectivity; H <sub>2</sub> activation; silane; iridium; chirality			
20. SUPPLEMENTARY NOTES			
21. ABSTRACT (Continue on reverse side if necessary and identify by block number) The complex IrBr(CO)(chiraphos), chiraphos = 2S,2S-bis(diphenylphosphino)butane, has been prepared, and its oxidative addition reactions with H <sub>2</sub> and Ph <sub>3</sub> SiH have been studied. The reaction with H <sub>2</sub> proceeds under kinetic control forming an initial pair of diastereomers in a 2:1 ratio followed by isomerization to a second, more stable pair of diastereomers which commence to form in a 2.4:1 ratio but exist at equilibrium in a 1.3:1 ratio. The kinetic differentiation observed for each pair of diastereomers results from the influence of chiraphos on the developing chirality at the metal center as the cis oxidative addition			

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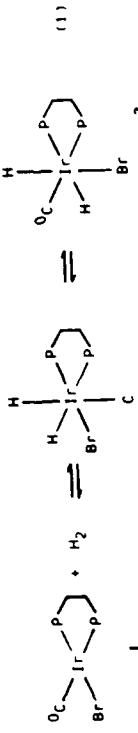
Differentiation and the Influence of Chiraphos on Metal-Centered Chirality  
in (cis) Oxidative Addition of Hydrogen and Triphenylsilane

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**Abstract:** The complex  $\text{IrBr}(\text{C}_6\text{H}_5\text{CH}_2\text{P}(\text{O})\text{Ph}_2)_2$ , chiraphos = 2S,3S-bis(tri- $\text{C}_6\text{H}_5$ phosphino)butane, has been prepared, and its oxidative addition reactions with  $\text{H}_2$  and  $\text{Ph}_3\text{SiH}$  have been studied. The reaction with  $\text{H}_2$  proceeds under kinetic control forming an initial pair of diastereomers in a 2:1 ratio followed by isomerization to a second, more stable pair of diastereomers which combine to form in a 2:4:1 ratio but exist at equilibrium in a 1:3:1 ratio. The kinetic differentiation observed for each pair of diastereomers results from the influence of chiraphos on the developing chirality at the metal center as the cis oxidative addition proceeds. A reaction coordinate diagram for the system is developed based on the observed kinetic and thermodynamic differentiations of the diastereomers. The oxidative addition of  $\text{Ph}_3\text{SiH}$  also takes place under kinetic control followed by isomerization. A 12:1 kinetic differentiation in the formation of the stable silyl hydride diastereomers occurs at 25°C due solely to the presence of chiraphos.

In the stereoselective, kinetically controlled oxidative addition of  $\text{H}_2$  to  $\text{IrBr}(\text{C}_6\text{H}_5\text{CH}_2\text{P}(\text{O})\text{Ph}_2)_2$ , 1, (dppe = bis(diphenylphosphinoethane), 1, both the kinetic isomer 2 and the thermodynamic isomer 3 form as racemates resulting from  $\text{H}_2$  approach to the metal center from above and below the  $\text{Ir}(\text{II})$  square planar complex. This is illustrated for 2 as **a** and **b** with  $\text{H}_2$  aligned parallel



to the  $\text{P}-\text{Ir}-\text{C}_6\text{H}_5$  axis of complex 1; formation of 3 proceeds similarly with  $\text{H}_2$  to  $\text{P}-\text{Ir}-\text{X}$ . In this communication, we describe studies in which the parallel to  $\text{P}-\text{Ir}-\text{X}$ .



optically active chiraphos, (2S,3S-bis(2-phenylphosphino)butane),<sup>2</sup> is used in place of dppe leading to kinetic and thermodynamic differentiation of the racemic products of  $\text{H}_2$  and  $\text{Ph}_3\text{SiH}$  oxidative addition. While the use of chiral diphosphines as catalysts for asymmetric hydrogenation has been widely investigated,<sup>3,4</sup> the present work represents the first study in which the effect of chiraphos on simple oxidative addition has been examined.

The complex  $\text{IrBr}(\text{C}_6\text{H}_5\text{CH}_2\text{P}(\text{O})\text{Ph}_2)_2$ , 4, prepared analogously to 1, reacts with  $\text{H}_2$  in acetone similarly to eqn 1) forming first diastereomers **5a** and **5b** with >99.5% stereoselectivity followed by slower formation of the more stable pair of diastereomers **6a** and **6b**. Figure 1 shows the hydride region of the  $^1\text{H}$  NMR spectrum upon initial oxidative addition and subsequent isomerization, and NMR data for the diastereomers are summarized below.<sup>5</sup> At -25°C, the kinetic diastereomer 5 form in a 2:1:1 ratio which remains constant for extended

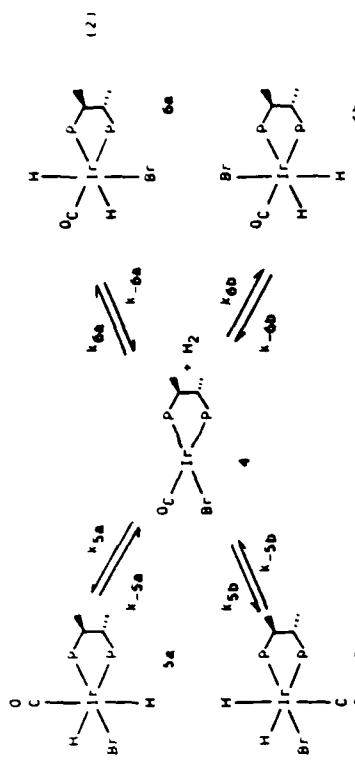
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periods of time. Just on warming to room temperature, changes within 5 min to 1:1 in the thermodynamic diastereomers **6** start to grow in. The isomerization of **5** to **6** follows first order kinetics with a rate constant for the disappearance of **5a** at  $4.9 \times 10^{-5} \text{ s}^{-1}$ . During early stages of the isomerization the observed ratio of **6a:6b** is 2.4:1, while at equilibrium the ratio is 1.3:1 with diastereomers **6** comprising 95% of the total hydride species present. At equilibrium, the ratio of **6a:6b** is 7.2:1.

To establish that the initial ratio of 2:1:1 seen for **5** at  $-25^\circ \text{ C}$  corresponds to kinetic differentiation of the diastereomers, **5** was formed at low temperature followed by replacement of  $\text{H}_2$  by  $\text{D}_2$ . After 1 hr at  $-25^\circ \text{ C}$  the amount and ratio of diastereomers of **5** showed no change, but upon warming to room temperature the hydride resonances rapidly diminished and disappeared within 1 hr, following first order kinetics with a rate constant of  $3.3 \times 10^{-3} \text{ s}^{-1}$  for diastereomer **5a**.

The experiments outlined above show that in addition to the stereoselective, kinetically-controlled  $\text{H}_2$  oxidative addition originally seen in eqn (1), diastereoselection for **5** and **6** occurs due solely to the influence of chiraphos on the developing chirality at the metal center as the cis oxidative addition proceeds. The kinetic differentiation expressed as  $\Delta\Delta G^\ddagger$  for **5a:5b** and **6a:6b** is 0.40 and 0.50 kcal/mole, respectively. From the experiment under  $\text{D}_2$ , we see that reductive elimination of  $\text{H}_2$  from **5** is rapid at room temperature, indicating that equilibrium between **5a** and **5b** is established prior to isomerization to **6**, and suggesting that the mechanism for isomerization involves reductive elimination to generate **4** followed by oxidative addition with  $\text{H}_2$  parallel to  $\text{p}-\text{Ir-X}$  forming **6**.

The proposed mechanism is shown as eqn (2). From the initially observed ratio of  $>200:1$  for **5:6** and eqn (3), we conclude that  $\Delta\Delta G^\ddagger$  between the formation of **5a** and **6a** must be  $>3.1$  kcal/mole. The thermodynamic differentiation between

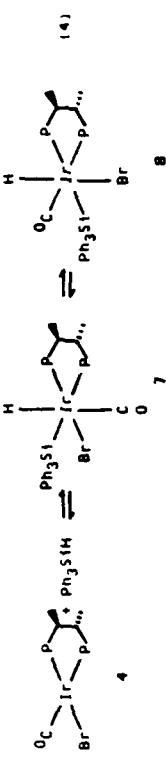


the diastereomers is obtained from the ratio of **5a:5b** as **6** starts to form, and the ratios **6a:6b** and **6a:5a** after equilibrium has been reached. A

$$\frac{[5a + 5b]}{[6a + 6b]} = e^{-(\Delta\Delta G^\ddagger_{5a-6b}/kT)} = \frac{(1 + k_{5b}/k_{5a})}{(1 + k_{6b}/k_{6a})} \quad (3)$$

reaction coordinate profile of the **4 + H<sub>2</sub>** system summarizing all of these results is given in Figure 2.

The oxidative addition of  $\text{Ph}_3\text{SiH}$  to **4** also proceeds stereoselectively under kinetic control in agreement with recent observations for silane addition to complex **1**.<sup>7</sup> The reaction occurs as shown in eqn (4) with the initial formation of **7** ( $>99:1$ ), followed by isomerization to the more stable diastereomers **8**.<sup>8</sup> The kinetic differentiation for **8** is striking as evidenced by the ratio for **8a:8b** of 12:1 during early stages of the isomerization, corresponding to  $\Delta\Delta G^\ddagger$  of 1.5 kcal/mole for the formation of the diastereomers. The eventual ratio of **8a:8b** at equilibrium is 1:1 indicating little thermodynamic differentiation between the diastereomers.



The isomerization of **7** to **8** most probably occurs by reductive elimination/oxidative addition similar to that shown in (2) since the reaction follows first order kinetics and reductive elimination of Ph<sub>3</sub>SiH from **7** is rapid relative to isomerization. The latter was shown by preparing **7** at -20° *c* followed by the addition of 5 eq MeCl<sub>2</sub><sup>1H</sup> which acts as an efficient trap for **4** by its oxidative addition to form LiBH<sub>2</sub>(SiMe<sub>2</sub>)<sub>2</sub>(CO)(chiraphos). Further studies using these and other silanes will be reported separately.

The results described above show that kinetic and thermodynamic differentiation of metal centered chirality in simple *cis* oxidative additions by chiraphos is significant.<sup>9</sup> The results also provide a sensitive probe to the transition state structure in these systems through observed differences in the extent of kinetic and thermodynamic differentiation for the diastereomers in these *cis* oxidative additions. Based on these differences, it appears that for both H<sub>2</sub> and Ph<sub>3</sub>SiH oxidative addition, the transition state in these reactions is not very product like.

**Acknowledgments.** We wish to thank the National Science Foundation (CHE-83-08064) and the Office of Naval Research for support of this work, and Johnson Matthey Co., Inc. for a generous loan of triplum salts.

#### References and Footnotes

- (a) Johnson, C. E.; Fisher, H. J.; Eisenberg, R. J. *J. Am. Chem. Soc.* **1983**, *105*, 1772. (b) Johnson, C. E.; Eisenberg, R. J. *J. Am. Chem. Soc.* **1985**, *107*, 3148.
- Fryzek, M. D.; Bosnich, B. *J. Am. Chem. Soc.* **1977**, *99*, 6262.
- (a) Knowles, W. S.; Sabacky, M. J.; Vineyard, B. D. *Adv. Chem. Ser.* **1974**, *112*, 274. (b) Keegan, M. H. *Pure Appl. Chem.* **1975**, *43*, 401, and references

therin. (c) Valentine, D. S.; Scott, J. W. *Synthesis* **1978**, *129*. (d)

Bosnich, B.; Roberts, N. K. *Adv. Chem. Ser.* **1982**, *196*, 337. (e) Brown, J. M.; Chaloner, P. A.; Parker, D. *Adv. Chem. Ser.* **1982**, *196*, 355.

(f) Chen, A. S. C.; Pluth, J. J.; Halpern, J. J. *J. Am. Chem. Soc.* **1980**, *102*, 5932. (b) Brown, J. M.; Chaloner, P. A. *J. Chem. Soc., Chem. Commun.* **1980**, 344. (c) Chub, P. S.; Roberts, N. K.; Bosnich, B.; Gerasinski, S. J.; Halpern, J. J. *Chem. Soc., Chem. Commun.* **1981**, 1218.

5. <sup>1H</sup> NMR data for hydride resonances in d<sub>6</sub>-acetone (*J*<sub>PH</sub> in Hz). **5a**: -8.95

(dd; 144.7, 12.9), -9.25 (dd; 21.6, 16.7). **5b**: -9.02 (dd; 145.9, 12.9),

-9.28 (~t; 20.8). **6a**: -8.71 (ddd; 127.1, 15.7, 4.3), -18.0 (mult). **6b**:

-9.50 (ddd; 128.8, 16.7, 4.9), -18.1 (mult).

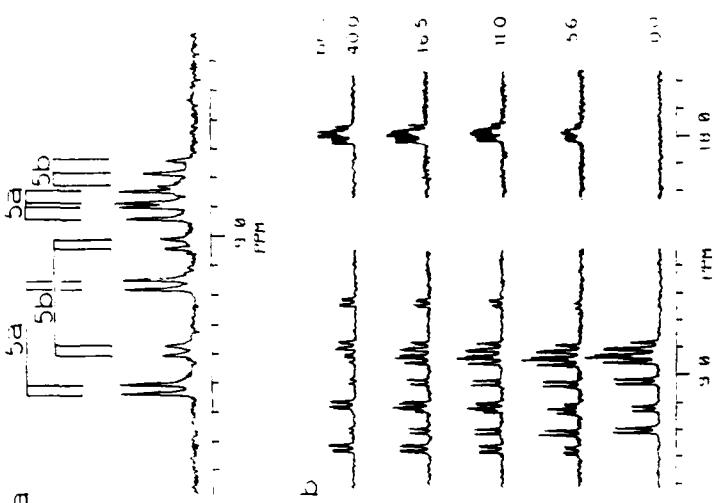
6. The assignment of metal-centered chirality for all of the diastereomers is based on an analysis of space-filling models of reactants and products for the oxidative addition reaction. These models, which are particularly informative for the silane oxidative addition, predict a kinetic preference for the  $\alpha$  configuration in the formation of both **5** and **6**, and little thermodynamic differentiation within each pair of diastereomers. These predictions must, of course, be confirmed by x-ray structural studies.

A different analysis has been presented by Brown and Chaloner who propose that diastereoselection of H<sub>2</sub> oxidative addition to Rh( $\alpha$ -benzamido)inamic acid(chiraphos)<sup>1</sup>, which was not observed directly, is determined by torsional strain in the Rh-chiraphos chelate ring. Brown, J. M.; Chaloner, P. A. in "Homogeneous Catalysts with Metal Phosphine Complexes", L. Pignolet, Ed., Plenum Publishing, New York, **1983**, 161-2. However, the importance of electronic factors in determining the diastereoselection in the Rh(chiraphos) system has not been examined as it has for the Br(CO)<sub>3</sub> complex.<sup>1</sup>

<sup>1</sup> Johnson, C. E.; Eisenberg, R. J. *J. Am. Chem. Soc.* **1985**, *107*, in press.

b. 1H NMR data for hydride resonances in  $d_6$ -acetone ( $\delta$  in ppm): 7.04 (dd, 16.8, 12.6), 7b: 8.49 (dd, 24.2, 13.7), 8a: 16.04 (dd, 13.7, 7.4), 8b: 16.14 (dd, 49.2, 5.3). Molecular models indicate that the configuration at the metal for diastereomer 8a which is kinetically preferred over 8b is a.

9. a. While diastereomeric cis dihydrides have been seen previously for  $(\text{LiH}_2\text{Dipamp})_2\text{IrA}$ , the stereoselectivity of the oxidative addition was not reported. Brown, J. M.; Dayll, F. M.; Lightowler, D. J. Chem. Soc., Chem. Commun., 1983, 414. b. For the oxidative addition of  $\text{H}_2$  to  $\text{[Ir(cod)(dipamp)]}_2\text{H}_2$ , only one set of hydride resonances was discernable. Presumably the diastereomers were not resolved. Crabtree, R. H.; Felkin, H.; Filibean-  
khen, I.; Morris, G. E. J. Organomet. Chem. 1979, **168**, 183.



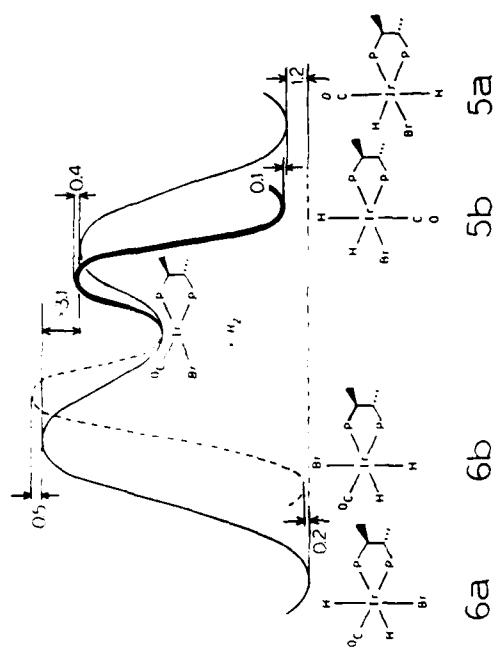


Figure 2. Reaction coordinate diagram for the system  $\text{IrBr}(\text{CO})(\text{chiraphos})$ . 4.

+  $\text{H}_2$ . Values of  $\Delta G$  and  $\Delta\Delta G^\ddagger$  are given in kcal/mole.

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